The combined red chloroform layer was washed with 4 *N* hydrochloric acid, 2 *N* sodium hydroxide solution, and water, and dried over $CaCl_2$. Acidification of the basic layer gave no precipitate. The chloroform layer was filtered and concentrated. The residue was chromatographed over alumina with benzene. The benzene was evaporated and the residue (200 mg, 57%) crystallized several times from alcohol, mp 267–270°.

Anal. Calcd for $C_{22}H_{14}S$: C, 85.16; H, 4.52; S, 10.32. Found: C, 84.86; H, 4.59; S, 10.23.

Uv: see Table IV. Mass spectrum: *m/e* 310 (parent peak), 311 (P + 1 = 28%, calcd 24.2%), 312 (P + 2 = 5%, calcd 4.4%), 309 (M − H), 308 (M − 2H), 265 (M − HCS), 155 (M^{2+}), 154.5 ($(M-1)^{2+}$), 154 ($((M-2)^{2+})$), 78, 45 (HCS^+), 44 (CS^+). Nmr (C_6D_6): τ 2.38–3.57 (m, 12 H), 4.63 (s, 1 H), 4.67 (s, 1 H).

Registry No.—Anthracene, 120-12-7; **5**, 268-77-9; **7a**, 22565-98-6; **7b**, 22565-99-7; **8**, 22566-00-3; **9**, 22566-01-4; **10**, 13395-89-6; **11**, 267-61-8; **12**, 267-65-2; **15**, 22566-39-8; **15** (2,4-dinitrophenylhydrazone), 22566-40-1; **19**, 22566-41-2; **20**, 477-75-8; **21**, 95-47-6; **22**, 22566-43-4; **23**, 5675-64-9.

Generation of *o*-Quinone Methides in Solution. Trimerization

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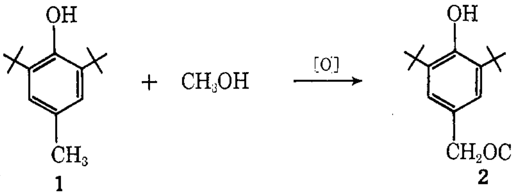
Three different 4-substituted 2,6-dimethylphenols were oxidized with various oxidizing agents such as silver oxide. The major product in each case is a trimer, which was characterized as arising from a trimerization of an *o*-quinone methide. The carbonyl group in the trimer was particularly unreactive, and the only easily run reaction was a reduction with acidic iodide, which not only cleaved a carbon–oxygen bond but caused an olefinic bond to shift out of conjugation.

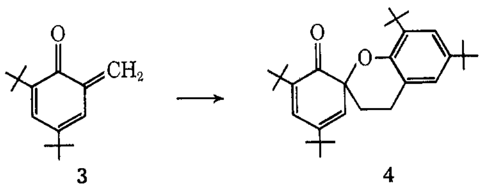
Quinone methides have been postulated as reactive intermediates in organic reactions for many years. A review has been written[1] which covers the literature to 1964. The isolation of a quinone methide with an unsubstituted methylene group has not been accomplished except at low temperatures[2,3] or in the case of highly hindered molecules.[4] Filar and Winstein[5] have demonstrated the existence of a *p*-quinone methide in dilute solution.

Identification of a quinone methide intermediate usually results from product studies. Filar and Winstein[5] oxidized **1** in methanol and formed **2** by trapping the *p*-quinone methide with the nucleophilic methanol.



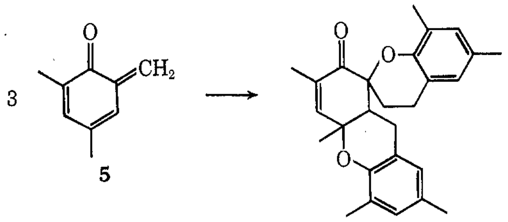
1 2

The second path involves the function of the *exo* methylene group as a dieneophile, which is illustrated by Waters'[6] work. Here the *o*-quinone methide **3** is acting as both the diene and dieneophile.



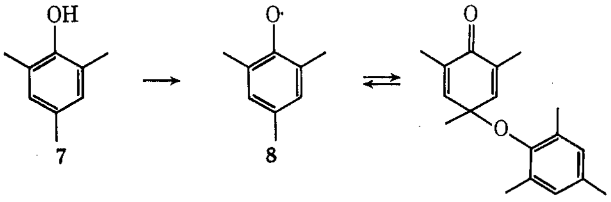
3 4

The only reports of isolated *o*-quinone methides is by Merijan, Shoulders, and Gardner,[3] who collected the quinone methide **5** at liquid nitrogen temperature. It then spontaneously trimerized upon warming, in a most unusual reaction.



5 6

The exact mechanism of the formation of the quinone methides is not known. The first step is the oxidation of the phenol **7** to the phenoxy radical **8**. This radical in turn reversibly dimerizes to the quinol ether **9**.



7 8 9

Becker has demonstrated that dimers of this type disproportionate to 1 mol of the phenol and 1 mol of the *p*-quinone methide.[7] A similar sequence probably occurs for *o*-quinone methides, but has not yet been demonstrated prior to this work.

This work was undertaken to examine some of the methods of generating *p*-quinone methides and to see whether they could be used to generate *o*-quinone methides in solution. The generality and scope of the reaction was to be examined.

Results and Discussion

In view of the results of Filar and Winstein,[5] who found that *p*-quinone methide formation was greatly

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[1] A. B. Turner, *Quart. Rev.* (London), **28**, 347 (1964).

[2] S. B. Cavitt, H. Sarrafizadeh R., and P. D. Gardner, *J. Org. Chem.*, **27**, 1211 (1962).

[3] A. Merijan, B. A. Shoulders, and P. D. Gardner, *ibid.*, **28**, 2148 (1963).

[4] A. Bistrzycki and C. Herbst, *Chem. Ber.*, **36**, 2335 (1903).

[5] L. J. Filar and S. Winstein, *Tetrahedron Lett.*, **25**, 9 (1960).

[6] R. F. Moore and W. A. Waters, *J. Chem. Soc.*, 243 (1954).

[7] H. D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

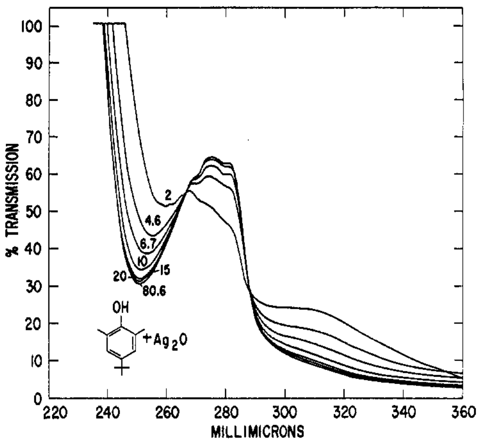
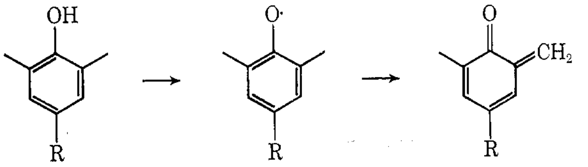


Figure 1.—Spectrum of a cyclohexane solution of 4-*t*-butyl-2,6-xylenol oxidized with silver oxide and scanned at the given intervals (time in minutes).

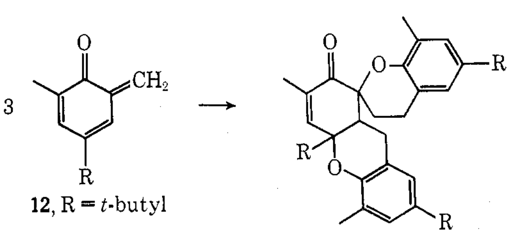
favored over *o*-quinone methide formation, it was necessary to block the *para* position of the phenol with a group which contained no α hydrogens to prevent both oxidative coupling and *p*-quinone methide formation. Three phenols were chosen, 4-*t*-butyl-, 4-phenyl-, and 4-methoxy-2,6-xylenols. Most of the work was done upon 4-*t*-butyl-2,6-xylenol because of its ready availability.

Trimer Formation.—When a phenol **10** is oxidized, the first-formed phenoxy radical **11** is converted into the *o*-quinone methide **12**. This transformation will be discussed in the mechanism section. The fate of **12** is primarily a reaction to restore the ring aromaticity. In the absence of other reactants **12** will react with itself.



10, R = *t*-butyl **11** **12**

For example, when R = *t*-butyl, an extremely rapid reaction occurs with silver oxide in benzene solution. This is shown by the conversion of the black silver oxide color to the light gray of the reduced form, mostly metallic silver. After the benzene is removed, a glass is obtained which finally yields a crystalline powder upon careful recrystallization. The obtained material has the structure **13** as confirmed by analysis, ir, nmr, and mass spectrometry. The mass spectrum of this trimer is discussed in the Experimental Section.



12, R = *t*-butyl

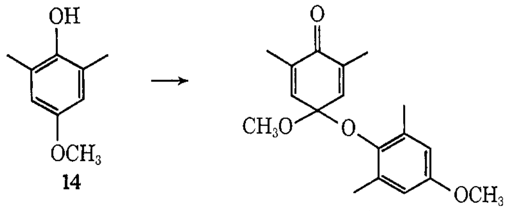
13

The nmr of compound **13** was in good agreement with the proposed structure. The methyl group on the cyclohexeneone ring was coupled with the vinyl proton as shown by double-resonance experiments. One unusual feature of the spectrum is a solvent effect upon one of the aromatic methyls. In carbon tetrachloride the two aromatic methyls appear at 2.04 and 2.07 ppm. When the solvent is deuteriochloroform the 2.07 ppm shifts to 2.16 ppm. No explanation for this behavior is yet available.

A number of oxidizing agents were used during this study. Silver oxide was superior to all others in yield and purity of the obtained trimer. Manganese dioxide, lead dioxide, and basic potassium ferricyanide would also give the trimer, although there were more side products formed with these latter reagents.

When experiments were run using less than stoichiometric amounts of the oxidizing agent only trimer and unreacted 4-*t*-butyl-2,6-xylenol were found. There was no evidence for dimeric species being formed. It would appear then that trimer formation is favored over other possible self reactions. This may be due to the driving force of ring aromatization.

There is a report by Martius and Eilingsfeld[8] that the oxidation of 4-methoxy-2,6-dimethylphenol with basic ferricyanide yields the quinone ketal **15**. In our hands this reaction did not yield the quinone ketal but rather the trimer **13** (R = OCH_3). In addition, the 4-phenyl-substituted monomer **10** (R = phenyl) also yielded a trimer **13** (R = phenyl).

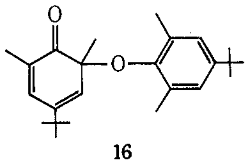


14 **15**

Mechanism.—The first step is the production of the phenoxy radical. Cook and Norcross[9] feel that the 2,6-di-*t*-butyl-4 isopropylphenoxy radical undergoes a second-order disproportionation, while Bennett[10] shows that the disappearance of the 4-methyl- or 4-ethyl-substituted radicals is first order. The evidence is clear that these radicals do convert into the free phenol and the *p*-quinone methide.

In our oxidation both uv and esr were used in an attempt to determine the mechanism of production of the *o*-quinone methide from the radical. A solution of 4-*t*-butyl-2,6-oxylenol in cyclohexane was oxidized with excess silver oxide and immediately filtered into a uv cell. The spectrum was run at various times and the results are shown in Figure 1.

The initial absorption at 312 mμ is ascribed to the short-lived quinol ether **16** based on the following evi-



16

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[8] C. Martius and H. Eilingsfeld, *Ann.*, **607**, 159 (1957).

[9] C. D. Cook and B. E. Norcross, *J. Amer. Chem. Soc.*, **78**, 3797 (1956); **81**, 1176 (1959).

[10] J. E. Bennett, *Nature*, **186**, 385 (1960).

dence. The absorption of *o*-quinol acetates is at 300–320 mμ, while *p*-quinol acetates absorb at 230–240 mμ.[11] Furthermore, if the 312-mμ absorption were due to the 4-butyl-2,6-xylenoxy radical, two peaks would by expected at 380 and 397 mμ equivalent in intensity to the 312-mμ peak.[12] The absence of these peaks eliminates the radical being responsible for the 312-mμ peak. It then was concluded that **16** is the intermediate giving rise to the 312-mμ absorption.

The disappearance of the 312-mμ peak and the appearance of the two peaks at 275 and 282 mμ have an isosbestic point. Since the peaks are due to the reappearance of the 4-*t*-butyl-2,6-xylenol, the decomposition of **16** must be rate controlling and proceed rapidly to the phenol.

The above data support the picture of a fragmentation of the quinol ether **16** into the free phenol and the *o*-quinone methide **12**. The quinone methide then trimerizes to **13** in a fast reaction. If we assume that the 40–50-mμ difference between *p*-quinols[11] and *p*-quinone methides[5] should carry over to the *ortho* species, we would expect an intense absorption for the *o*-quinone methide around 352–362 mμ. This was not observed and the conclusion is that the *o*-quinone methide is too short lived at 25° for spectral observation.

The expected mixture from 1 mol of **16** would be 0.5 mol of 4-*t*-butyl-2,6-xylenol and one-third of 0.5 mol of trimer. A synthetic mixture of these two components was made and in Figure 2 it can be seen that the uv of this mixture corresponds well with the final result in Figure 1. Also in Figure 2 the uv of 1 mol of 4-*t*-butyl-2,6-xylenol is given, showing the similarity of peak height though the quantity of material is halved.

The mechanism is even more complicated, for when an esr was run on a moderately concentrated solution of the oxidized phenol in cyclohexane, a seven line, long-lived spectrum was observed. The two smallest peaks were not resolved, but the peak height ratio of the five largest peaks confirmed the seven-line spectrum. The splitting constant of 6.2 G compares with 6.1 G obtained by Becconsall, Clough, and Scott for the splitting by the *o*-methyl protons on 4-*t*-butyl-2,6-xylenoxy radical.[13] This radical persisted long past the point at which the absorption at 312 mμ had disappeared. Obviously, the radical is present even though it is not detected by ultraviolet spectrum. The relatively constant amount of the radical suggests that it may not be in equilibrium with the quinol ether but has some low threshold concentration and decays only slowly, perhaps by another mechanism.

Reduction of the Trimer.—The steric hindrance of the 4-*t*-butyl group is observed in several ways. The difficulty of crystallizing of the trimer **10** has already been mentioned. In addition to this there is another unique reaction.

When the trimer **13** is treated with acidic iodide, a new trimer is formed along with the liberation of iodine. Titration of the iodine with thiosulfate revealed that the equivalent of two hydrogens had been added. The carbonyl had shifted from 1700 to 1720 cm^{-1} in the infrared, and the conjugated carbonyl in the ultraviolet at λ_{max}^{EtOH} 297 mμ (ε 3000) had disappeared. These suggest that the double bond was reduced. However, there is a strong hydroxyl band in the infrared. This suggests that a carbon–oxygen bond had been reduced. The nmr spectra, along with the mass spectrum of the new trimer, proved that it possessed the structure **17**, where the carbonyl was deconjugated simultaneously with cleavage of the aryloxy bond in the 4 position of the cyclohexenone ring.

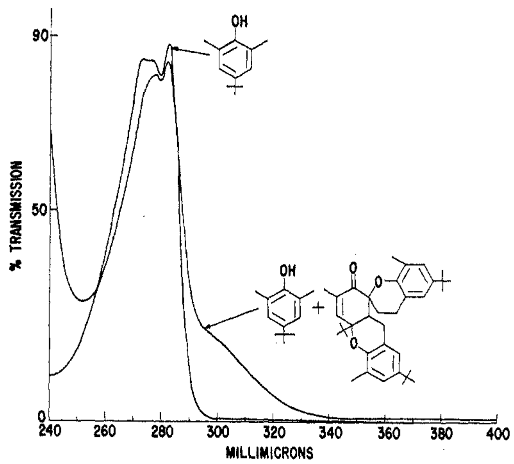
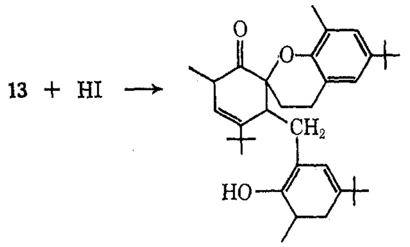


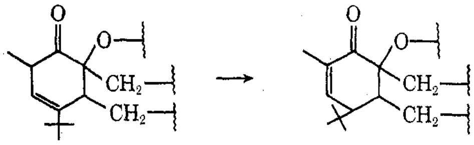
Figure 2.—Spectrum of 4-*t*-butyl-2,6-xylenol superimposed on the synthetic mixture which would result from conversion of the phenol into the phenoxy radical, followed by the subsequent reactions.



17

The reason for this unusual deconjugation is apparently steric requirements of the *t*-butyl group. The analogous trimer **13** (R = methyl) was obtained[14] and does not undergo iodide reduction. Numerous attempts to use acid or base catalysis to conjugate the double bond and the carbonyl failed. The 3 kcal of resonance energy gained by conjugation[15] is evidently not enough to override the steric effect.

A careful examination of the models of the two systems **18** and **19** was made and there were no obvious large steric differences.



18 **19**

There are two conformers for each ring; it is true that the *t*-butyl group in **19** is forced into a slightly hindered axial position in one conformer, but this does not seem to be enough to account for the prevention of conjugation.

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[11] A. J. Waring, *Advan. Acycl. Chem.*, **1**, 188 (1967).

[12] E. J. Land and G. Porter, *Trans. Faraday Soc.*, **59**, 2016 (1963).

[13] J. K. Becconsall, S. Clough, and G. Scott, *ibid.*, **56**, 459 (1960).

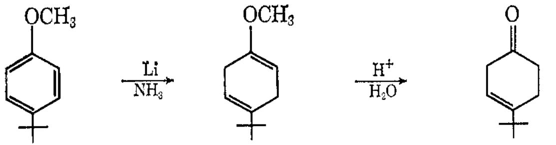
[14] A sample of 3,5-dimethylquinone-2-methide trimer was obtained through the courtesy of Professor P. D. Gardner.

[15] G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1955, p 85.

Other reductions upon the original trimer were attempted. In most cases the relatively hindered carbonyl and olefin stubbornly refused to reduce. Atmospheric and moderate pressure hydrogenations with a variety of catalysts failed to accomplish any reduction. Of the chemical reducing agents tried only lithium aluminum hydride achieved any reduction and this only at prolonged heating. The carbonyl group was reduced to the corresponding alcohol.

As a further testimony to the hindered nature of the carbonyl group, it was not possible to made any derivatives of **13**.

Wilds and Nelson[16] have prepared 4-cyclohexyl-3-cyclohexenone by a Birch reduction and found that its 2,4-dinitrophenylhydrazone derivative conjugated with acid catalysis. In this work the analogous 4-*t*-butyl-3-cyclohexenone **22** was prepared to see whether the *t*-butyl group exerts any influence upon the conjugation of the cyclohexenone. The following sequence of reactions was used.



20 21 22

The ketone **22** could not be purified by distillation. Infrared analysis showed the distilled ketone to be 24% conjugated. The pure unconjugated ketone was successfully purified by preparative vpc. It was then refluxed in methanol acidified with concd HCl and reisolated. After 1 hr it was 41% conjugated, and after 2 hr it was 63% conjugated. Apparently even without the additional group present in the reduced trimer conjugation of this olefin is much slower than the usual cyclohexenone, and this is ascribed to the presence of the *t*-butyl group.

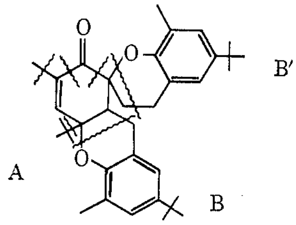
A better model for the reduced trimer would be 4-*t*-butyl-2,6-dimethylanisole, but Birch reduction of this material gave only methyl ether cleavage, not ring reduction.

Experimental Section

Ag_2O Oxidation of 4-*t*-Butyl-2,6-dimethylphenol.—A mixture of silver oxide (7.5 g, 0.033 mol) and benzene (100 ml) was stirred and flushed with nitrogen. To this mixture was added 4-*t*-butyl-2,6-dimethylphenol (5.34 g, 0.03 mol). The solution was stirred for 18 hr. The benzene was filtered to remove the silver salts and dried ($MgSO_4$). The benzene solution was again filtered and the benzene removed on a film evaporator. A yellowish glass was obtained which was taken up in hot methanol and subsequently cooled. The material was difficult to crystallize and alternate heating and cooling was usually necessary to induce crystallization. The quinone methide trimer (**13**, R = *t*-butyl) was obtained as white crystals: mp 146.5–148°; 3.85 g, 72%. Further recrystallizations gave pure trimer: mp 148–149°; ir 1700 cm^{-1} (C=O); nmr (CCl_4) τ 1.20, 1.23 (3-*t*-butyl), 1.51, coupling 2.04 (2-methyl), 2.07 (methyl, 2.16 in $CDCl_3$), 6.29 (vinyl), 6.72, 6.90 ppm (aromatic). The 6-methylene and 1-methine protons were diffuse and not readily assigned.

Anal. Calcd for $C_{36}H_{48}O_3$: C, 81.8; H, 9.1; ml wt, 528. Found: C, 81.9; H, 9.3; mol wt, 504.

The mass spectrum was run on the trimer **13** on an AEI MS-9 instrument with a heated probe. The favored fragmentation patterns are shown with the molecular ion *m/e* 528, and with the *m/e* 472 being the base peak. This corresponds to the ready loss of one *t*-butyl group, the group at A. The second largest peak is *m/e* 352, which corresponds to the loss of an *o*-quinone methide unit, one of the groups at B. All major peaks could be assigned to the given structure.

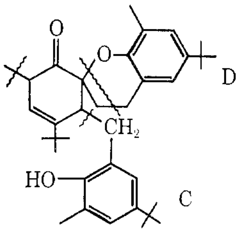


13

HI Reduction of Quinone Methide Trimer (13).—The trimer (**13**, R-*t*-butyl) (2.12 g, 0.004 mol) was dissolved in glacial acetic acid (60 ml). Hydriodic acid (57%, 4 ml) was added and the mixture allowed to stand for 2 hr. The mixture was then poured onto ice; the yellow solids were filtered. These solids were recrystallized from acetone–water yielding the reduced trimer **17**: 1.54 g, 73%; mp 198–200°.

Anal. Calcd for $C_{36}H_{50}O_3$: C, 81.4; H, 9.4; mol wt, 530. Found: C, 81.6; H, 9.4; mol wt, 516.

The mass spectrum of the reduced trimer **17** showed the molecular ion at *m/e* 530. The base peak is *m/e* 177, which corresponds to the ion arising from the benzellic group at C. The next most abundant ion is *m/e* 354, which may be assigned to the loss of D from **17**. *t*-Butyl groups are not lost so readily as in **13**.



17

LiAlH Reduction of Trimer 13—In a 500-ml round-bottom flask with the usual equipment were placed freshly distilled tetrahydrofuran (100 ml, from CaH_2) and lithium aluminum hydride (2.0 g). While this solution was kept at room temperature the trimer (**13**) (1.06 g, 0.002 mol) in THF (50 ml) was added slowly. The slurry was stirred for 0.5 hr and then refluxed for 2 hr. The reaction was cooled and a 10% water in THF solution (50 ml) was added slowly, followed by 6 *N* HCl (100 ml) and benzene (150 ml). The organic layer was separated, washed with water, and dried ($MgSO_4$). The solvent was removed on a film evaporator leaving a yellow gum, which when recrystallized from acetone–water gave white crystals: mp 87–90°; yield 0.35 g (35%).

Anal. Calcd for $C_{36}H_{50}O_3$: C, 81.4; H, 9.4; mol wt, 530. Found: C, 81.1; H, 9.4; mol wt, 538.

$K_3Fe(CN)_6$ Oxidation of 4-Methoxy-2,6-dimethylphenol.—A solution of 4-methoxy-2,6-dimethylphenol[17] in pentane (150 ml) was cooled to 15° and shaken with a water solution (25 ml) of potassium ferricyanide (5 g) and potassium hydroxide (2 g). After 2 min the pentane became yellow. The organic layer was separated, washed with water, and dried ($MgSO_4$). The pentane was removed under vacuum and the orange oil which remained taken up in methanol. Cooling the methanol yielded 0.2 g (20%) of yellow solids, mp, 170°. Further methanol recrystallization gave a pale yellow solid trimer **13** (R = CH_3), mp 172–175°.

Anal. Calcd for $C_{27}H_{30}O_6$: C, 72.0; H, 6.7; CH_3O, 20.7; mol wt, 450. Found: C, 72.0; H, 6.9; CH_3O, 20.8; mol wt, 420.

Ag_2O Oxidation of 4-Methoxy-2,6-dimethylphenol.—A benzene solution (150 ml) of 4-methoxy-2,6-xylenol (4 g) was purged with nitrogen. To this solution was added silver oxide (20 g), and the mixture was stirred for 4 hr. The solids were filtered; the benzene was removed on a film evaporator. The residual yellow gum was dissolved in hot methanol (15 ml) and the solu-

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[16] A. L. Wilds and N. A. Nelson, *J. Amer. Chem. Soc.*, **75**, 5360 (1953).

[17] W. Reeve and A. Sadle, *ibid.*, **72**, 3252 (1950).

tion cooled. The pale yellow crystals of trimer (**13**, R = CH_3O) were filtered: yield 2.0 g (50%), mp 167–169°.

This material was identical with the trimer prepared by the ferricyanide oxidation.

Ag_2O Oxidation of 4-Phenyl-2,6-xylenol.—A mixture of benzene (75 ml), silver oxide (5.0 g, 0.022 mol), and 4-phenyl-2,6-xylenol (3.96 g, 0.02 mol) was stirred for 3 hr. The solution was dried ($MgSO_4$). The benzene was removed on a film evaporator and the residue recrystallized from acetone–water. Light yellow solids were obtained (3.5 g, 88%).

Several recrystallizations gave white crystals, mp 198–200°, of the trimer **13** (R = C_6H_5).

Anal. Calcd for $C_{42}H_{36}O_3$: C, 85.8; H, 6.1; mol wt, 588. Found: C, 85.9; H, 6.0; mol wt, 609.

4-*t*-Butylanisole.—Commercial 4-*t*-butylphenol was methylated with dimethyl sulfate after conversion into its salt with sodium. The yield was 81% colorless anisole, bp 51° (0.7 mm).

Li–NH_3 Reduction of 4-*t*-Butylanisole.—The general procedure of Wilds and Nelson[16] was followed for the Birch reduction of 4-*t*-butylanisole.

A 500-ml three-necked flask was insulated with vermiculite. The flask was charged with 4-*t*-butylanisole (8.2 g, 0.05 mol) and anhydrous ether (75 ml). Anhydrous ammonia (100 ml) was distilled into the flask, which was equipped with a Dry Ice–acetone condenser. Lithium wire (2.2 g, 24 g-atoms) was added over 5 min. After 0.5-hr stirring of the solution, methanol (20 ml) was added slowly. When the ammonia had evaporated the ether solution was washed with water and dried ($MgSO_4$). The product remaining after removal of the ether was distilled, yielding 5.2 g (63%) of the colorless dihydroanisole, bp 43° (0.4 mm).

Anal. Calcd for $C_{11}H_{18}O$: C, 79.5; H, 10.8; mol wt, 166. Found: C, 79.7; H, 10.5; mol wt, 178.

Hydrolysis of 2,5-Dihydro-4-*t*-butylanisole.—A cold (0–5°) mixture of sulfuric acid (25 ml) and water (75 ml) was added dropwise to a cold (5°) solution of 2,5-dihydro-4-*t*-butylanisole (2.8 g) in benzene (100 ml). This mixture was allowed to warm to 25° after the addition of the acid was complete. The layers were separated; the benzene layer was washed with water, sodium bicarbonate solution, and water, then dried ($MgSO_4$). The yellow oil obtained after removal of the benzene was distilled, giving 1.9 g (74%) of 4-*t*-butyl-3-cyclohexenone, bp 45° (0.4 mm), $n^{15}D$ 1.4816.

Anal. Calcd for $C_{10}H_{16}O$: C, 79.0; H, 10.5; mol wt, 152. Found: C, 78.8; H, 10.2; mol wt, 166.

The infrared spectrum of this material revealed that it consisted of both the conjugated (24%) and unconjugated ketones (76%). Preparative vpc was used to obtain a small but pure sample of 4-*t*-butyl-3-cyclohexenone.

Conjugation of 4-*t*-Butyl-3-cyclohexenone.—Samples of the pure ketone were refluxed for 1 and 2 hr in absolute methanol containing ~1% concentrated HCl. The ketone was reisolated by extraction into ether, washing with water, dilute base, and water, and then drying. The 1-hr sample gave 41% conjugation, while the 2-hr sample gave 63% conjugation. The reaction is evidently slow.

2,4-Dinitrophenylhydrazone of 4-*t*-Butyl-3-cyclohexeneone.—The method of Shriner and Fuson[18] was used. A yield of 0.155 g (29%) of the purified dinitrophenylhydrazone was obtained from 0.25 g of the ketone, mp 163–165°.

Anal. Calcd for $C_{16}H_{20}O_4N_4$: C, 57.8; H, 6.0; N, 17.0; mol wt, 332. Found: C, 57.7; H, 6.1; N, 17.0; mol wt, 332.

Registry No.—**13**, R = *t*-butyl, 22566-50-3; **13**, R = CH_3O, 21856-90-6; **13**, R = C_6H_5, 22566-51-4; **17**, 22566-52-5; **21**, 22566-53-6; **22**, 5234-62-8; 2,4-dinitrophenylhydrazone of **22**, 22566-55-8.

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Chlorination of Aromatic Systems with Trichloroisocyanuric Acid under Polar and Free-Radical Conditions[1]

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Trichloroisocyanuric acid (I) was found to be an effective laboratory reagent for nuclear or side-chain halogenation of aromatic systems. Chlorination of common aromatic, polynuclear, and mixed aromatic–aliphatic systems was investigated. A charge-transfer intermediate appears to be involved in the reaction.

The use of trichloroisocyanuric acid (1,3,5-trichloro-2,4,6-trioxohexahydro-*s*-triazine) as an allylic halogenating agent was described by Ziegler,[3] and we have previously reported examples of α halogenation of saturated cyclic ethers.[4] N-Halogen compounds, such as N-bromosuccinimide, N-chlorosuccinimide, N-bromoacetamide, etc., were previously described as nuclear[5] and side-chain[6] halogenating agents. The use of trichloroisocyanuric acid in this capacity has not been described. As part of our continued study of the use of this reagent as a convenient laboratory substitute for chlorine, we now report its reactions with a number of common aromatic compounds. Other examples of the synthetic variety offered by this reagent are its use as a hypohalogenating agent[4] and the novel and direct conversion of ethers into esters.[7]

The reaction of trichloroisocyanuric acid (Scheme I) with benzene in the presence of anhydrous ferric chloride or 50% aqueous sulfuric acid as catalytic reagents yielded chlorobenzene. It is analogous to the reaction of benzene with molecular chlorine, which requires Lewis acid catalysis. In addition, naphthalene also required Lewis acid catalysis to effect good yields of the 1-chloro product, and only small amounts of product were obtained when no catalyst was employed

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[1] Taken in part from the M.S. theses of D. A. Beal and W. P. Duncan, Kansas State College of Pittsburg, 1968 and 1966, respectively.

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